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Fluorescent carborane-vinylstilbene functionalised octasilsesquioxanes: synthesis, structural, thermal and photophysical properties

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Abstract

A new set of four different fluorescent boron-rich hybrids based on an octasilsesquioxane core (T_8) are presented herein. The syntheses have been carried out starting from styrene-containing *ortho*- and *meta*-carboranes and an adequately substituted octasilsesquixane derivative (*p*-BrStyrenylOS) via Heck coupling reaction. The carborane clusters are attached to the T_8 core through *para*-substituted stilbene spacers, which act as the main electronic donor of the molecule and as a result are responsible for the photoluminescence properties of the hybrids. These have been assessed in DCM solution, concluding that the presence of the carborane clusters plays a key role in the increase of the fluorescence emission displayed by the hybrids. A comparative study of different substituents (H, Me or Ph) linked to the adjacent carbon atom of the *ortho*-cluster revealed that the unsubstituted *o*-carborane derivative (**POSS-H**) has a much higher quantum yield in solution (Φ_F = 59%) than its two counterparts. Besides, a comparison between two hybrids containing phenyl-substituted *ortho*- (**POSS-Ph**) and *meta*-carborane (**POSS-*m*Ph**), demonstrated a significant higher emission enhancement by the latter, backing the results we have previously reported for similar systems. In solid state, the emission is largely quenched in all cases (Φ_F = 4 to 7%) as well as bathochromically shifted due to considerable intermolecular interactions. Finally, the thermal resistances of these hybrids were tested by TGA under inert atmosphere, unveiling weight losses as low as 15.8 % and proving that the attachment of the carborane moieties to the T_8 core outstandingly improves the thermal stability of the final POSS.

Introduction

Octasilsesquioxanes (T_8) are compounds of general formulae $[RSiO_{1.5}]_8$ with a 3-D scaffold that are easy to synthesise and exhibit versatility in functionality, high robustness and thermal stability.[1] They can be easily modified to control the nanostructure assembly and tailor chemical properties such as solubility in organic solvents, oxidative stability and catalytic activity as well as mechanical, electrical, optical or electronic properties.[1d, 2] These exceptional characteristics make silsesquioxane-based materials very useful for a wide variety of applications,[3] including thermally and chemically resistant polymers and ceramics,[4] as flame retardants,[5] catalysis,[6] nanomedicine,[7] emitting layers in OLEDs,[8] among others.

On the other hand, icosahedral boron clusters are compounds with three-dimensional electron delocalisation that have unique properties such as highly polarisable σ-aromaticity,[9] thermal and chemical stability,[10] geometrical diversity,[11] low toxicity and special electronic properties,[9b] making them exceptional candidates for applications in biomedicine and materials science.[10d, 12] The recent use of carborane clusters in materials science has been focused on the development of polymers,[12a] boron-rich dendrimers,[13] liquid crystals,[14] non-linear optics,[15] and more recently, luminescent materials.[16] Our group has also contributed to the advancement of luminescent molecular systems, in which *o*-carborane derivatives linked to different fluorescent π-conjugated organic systems have been described and their emission properties evaluated.[10c, 17]

In the course of these studies we have developed a set of fluorescent systems which combine the particular properties of boron, organic π-conjugated systems and silsesquioxanes, i.e. carboranyl-styrene decorated polyhedral oligomeric silsesquioxanes

(POSS); these systems were synthesised using cross-metathesis of styrene-containing carboranes with octavinylsilsesquioxane (OVS) catalysed by Grubbs' first generation catalyst.[10c] We evaluated the photophysical behaviour of these compounds in solution, by modifying the substituent linked to the second carbon cluster (C_c) for *o*-carborane derivatives and compared them with the free styrenyl-carborane species. The results showed that after grafting the styrenyl-carborane precursors (**1-3** in Scheme 1) to the OVS core, large Stokes shifts and significant differences in the fluorescence emission intensity were found; i.e. the phenyl-*o*-carborane-containing POSS compound exhibited the highest fluorescence quantum yield ($\Phi_F = 44$ %), whereas its precursor was not fluorescent at all, due to a quenching induced by a charge transfer (CT) process.[10c] These results suggested that modification of the substituent bound to the C_c can tailor the final luminescent properties of the POSS hybrid. Moreover, the difference of the fluorescence before and after grafting was attributed to the spatial ordering induced by the OVS core that eases interactions that otherwise would not occur.

Motivated by our previous remarkable results, we report herein the syntheses and spectroscopic characterisation of a new set of POSS hybrids with extended conjugation containing *ortho* and *meta*-carborane-substituted vinylstilbenes. Regarding the potential of silsesquioxanes for OLEDs and photovoltaic applications,[8a, 18] our aim is to evaluate the optical and photophysical properties of these hybrids, focusing on the influence of the cluster's isomer and the substituent at their second C_c, both in solution and solid state. The results are discussed and supported with density functional theory (DFT). The thermal stability of the new POSS hybrids is also investigated.

Results and Discussion.

Synthesis and characterisation of hybrids. On one hand, the starting carboranyl derivatives **1**-**3** were prepared from *o*-carborane, Me-*o*-carborane and Ph-*o*-carborane respectively, whereas compound **4** was prepared from Ph-*m*-carborane, all of them following literature procedures (see Scheme 1).[17b, 17e] On the other hand, octa(*p*-bromostyrenyl)silsesquioxane (*p*-BrStyrenylOS) was prepared following the procedure reported by Laine et al.,[19] and serves as the main core that is functionalised with the aforementioned carboranyl derivatives **1-4** via Heck reaction. These reactions were carried out in 1,4-dioxane solutions of **1-4** with *p*-BrStyrenylOS using N,N-dicyclohexylmethylamine (NCy$_2$Me) as a base and [Pd(^{t}Bu$_3$P)$_2$] and [Pd$_2$(dba)$_3$] as co-catalysts at 85ºC, leading to the formation of **POSS-H**, **POSS-Me**, **POSS-Ph** and **POSS-*m*Ph**, respectively (Scheme 1). POSS-hybrids were isolated by precipitation from a mixture of THF/methanol without further purification in a 62, 66, 43 and 65 % yield respectively (Scheme 1). The reaction was monitored by ^{1}H NMR and the complete conversion was confirmed upon change in the aromatic proton resonance distributions as well as in the chemical shift of the peak corresponding to the Si-C*H* proton (Fig. S1).
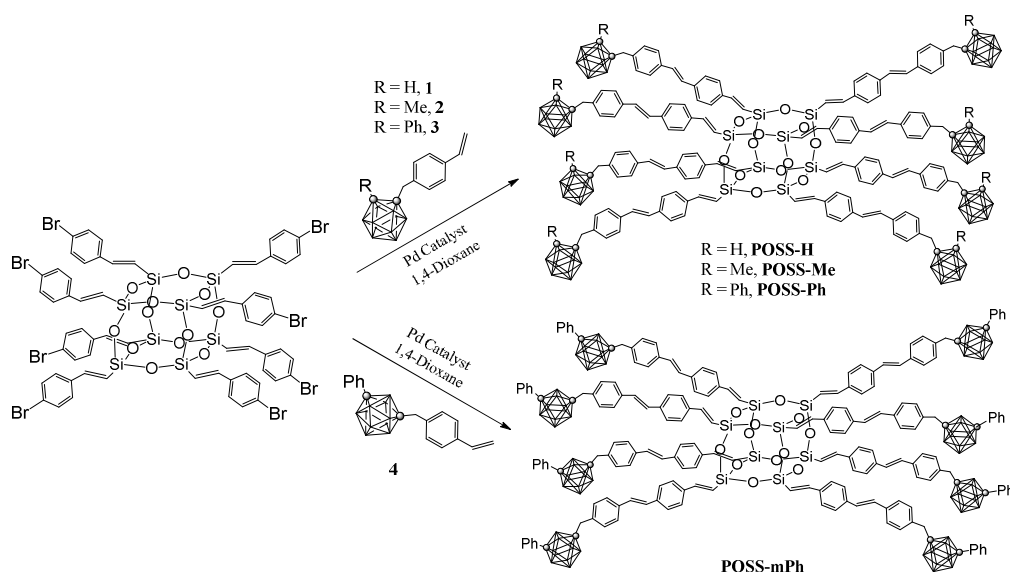
Scheme 1 Synthesis of POSS containing carboranyl-substituted vinylstilbenes.

All hybrids were characterised by ATR-IR, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$, ^{11}B, $^{11}B\{^1H\}$ and ^{29}Si NMR, UV-Vis and fluorescence spectroscopies as well as elemental analyses. The IR spectra for *o*-derivatives, **POSS-H**, **POSS-Me** and **POSS-Ph**, show the characteristic $\upsilon(B\text{-}H)$ strong band around 2580 cm^{-1}, whereas the *m*-derivative **POSS-*m*Ph** shows this band at 2594 cm^{-1}. Furthermore, a band near 1600 cm^{-1} attributed to the $\upsilon(C=C)$ and the typical broad band between 1000–1200 cm^{-1} due to the Si-O bond were observed for all compounds. ^1H NMR spectra for all new POSS show aromatic resonances in the 7.75-6.85 ppm region and the C*H*-Si resonance appears as a doublet ($^3J_{H\text{-}H} = 21$ Hz) between 6.37 and 6.42 ppm, slightly downfield with respect to the starting *p*-BrStyrenylOS at 6.27 ppm (Fig. S1). In addition, the shift of the -C*H$_2$*- proton resonances for *o*-derivatives depend on the second C_c substituent (H, Me or Ph), being upfield in the case of Ph that is in agreement with previous results.[17e] Despite the presence of one C_c-Ph group in **POSS-*m*Ph**, the -C*H$_2$*- proton resonance appears shifted downfield respect to **POSS-Ph**, since in the former there is no influence of the ring electronic current on

these protons (Fig. S1). Additionally, the singlet at 3.27 ppm in **POSS-H** is attributed to the C_c-H proton. The $^{11}B\{^1H\}$ NMR spectra of POSS containing Me- or Ph- substituents in the cluster show overlapped boron resonances with patterns 2:8 or 2:6:2 in the -3.85 to -12.97 ppm range. However, for the more asymmetrically substituted *ortho*-carborane in **POSS-H**, the pattern is 1:1:4:2:2 in the region from -2.9 to -13 ppm. In all these cases the corresponding ^{11}B NMR show the coupling between the ^{11}B and ^1H nuclei (see experimental section). The $^{13}C\{^1H\}$ NMR spectra show the aromatic and vinylic resonances between 149 and 117 ppm for all compounds and the peaks in the region 40-44 ppm are attributed to the methylene groups. C_c-C resonances are present in the 74-82 ppm interval, except the ones attributed to the C_c-H in **POSS-H**, which appear at 59.40 ppm. Elemental analyses have confirmed the structures of the POSS compounds. The ^{29}Si NMR of all the final POSS show an individual peak between -78.14 and -78.18 ppm that corroborate the total functionalization of the cage; these resonances are slightly downfield respect to the signal at -78.48 ppm obtained here for the starting *p*-BrStyrenylOS, in agreement with previous results reported by Laine et al.[19] (see details in the Experimental Part and SI).

Molecular Conformation. To determine the conformation of the compounds, density functional theory (DFT; employing the B3LYP functional) studies of **POSS-H** within the D_2 point group were performed, allowing full conformational freedom for each vinylstilbene-carborane ligand, but at the same time imposing identical conformational environment. Geometry optimisation of **POSS-H** resulted in planar vinylstilbenes with minimised (π-π) interactions between them (see Fig. 1 and SI). This will be of crucial importance for the understanding of the optical properties, *vide infra*.
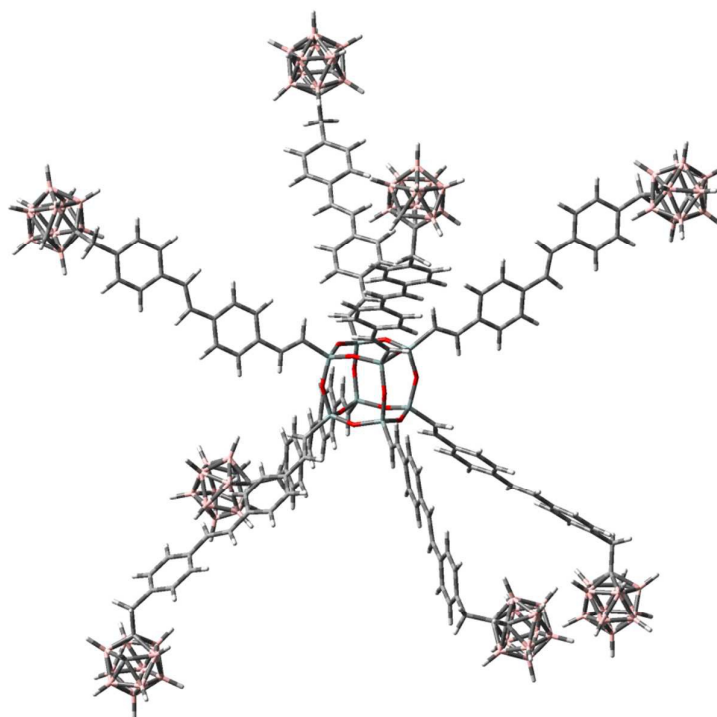
Fig. 1 DFT-optimised structure of **POSS-H.**

UV-Vis Absorption and Fluorescence. All POSS hybrids show somewhat vibronically
structured UV-Vis absorption spectra in dichloromethane (DCM) with λ_{max} near 338 nm
(3.67 eV; see Fig. 2 and SI), which matches to the carborane-free (p-methyl-stilbene-
vinyl)$_8$OVS system in THF and DCM reported by Laine's group.[19] Furthermore, in
these compounds the fluorescence is also vibronically structured, similar to what was
reported on free carborane-stilbenes,[17b] and distyrylbenzene (DSB).[20] Both for *trans*-
stilbenes and DSB it was shown that their fluorescence spectra were better resolved
compared to the absorption ones (Fig. 2 and SI). This is due to the shortening of the
single bonds upon electronic excitation, which steepens the torsional potential around
the vinyl-phenyl single bonds in the first excited singlet state S_1 compared to the
electronic ground state S_0.[21] This is apparently also the case in the here reported
compounds. The similarity of the fluorescence spectrum of the current **POSS-H**

compound with that of the free carborane-stilbene molecule indicates that the internal vibrational degrees of freedom are only slightly affected by the POSS cage arrangement.

The molar extinction coefficient of **POSS-H** is as high as $\varepsilon_m = 58.1 \cdot 10^4$ M^{-1} cm^{-1}, while for those hybrids containing C_c-substituted carboranes ε_m is somewhat lower (Table 1), which might suggest some aggregation in the latter.[20] In fact, compared to **POSS-H**, an unusual broadening of fluorescence in the red part of the spectra is observed for **POSS-Me**, **POSS-Ph**, and **POSS-mPh** (Figure 2), indicative of intermolecular interactions,[20] and which clearly correlates with the lowering of ε_m.

Noticeably, the fluorescence quantum yield for **POSS-H** is very high, $\Phi_F = 59$ %, and has a lifetime (τ_F) of 0.82 ns, from which a radiative rate of 0.65 ns^{-1} is calculated, see Table 1. This is similar to what is expected for vinylstilbene itself,[22] and indicates that only small excitonic interactions between the vinylstilbene branches are observed within the compound.[22] Indeed, according to the TD-DFT calculations, only very weak H-type interaction[20] is found with a forbidden lowest singlet state (S$_1$), separated by only 0.06 eV from the state with highest oscillator strength (3.43 eV, $f = 3.45$). Based on these calculations, Herzberg-Teller type coupling (i.e. coupling of the symmetry-forbidden electronic state to a close-by allowed one via a vibration of appropriate symmetry) should be highly efficient and the emitting state should be allowed in accordance with the experimental results.

It should be stressed in this context that a clear enhancement in the quantum yield of **POSS-H** is observed compared to (p-methyl-stilbene-vinyl)$_8$OVS ($\Phi_F = 22$ %) in DCM,[19] in which the -CH$_2$-o-carborane moieties have been replaced by methyl groups. The difference in Φ_F might be due to the fact that in this system the absence of the

sterically demanding carborane moieties permits stronger (excitonic) interactions between the vinyl-stilbene branches, which partly quench the fluorescence.
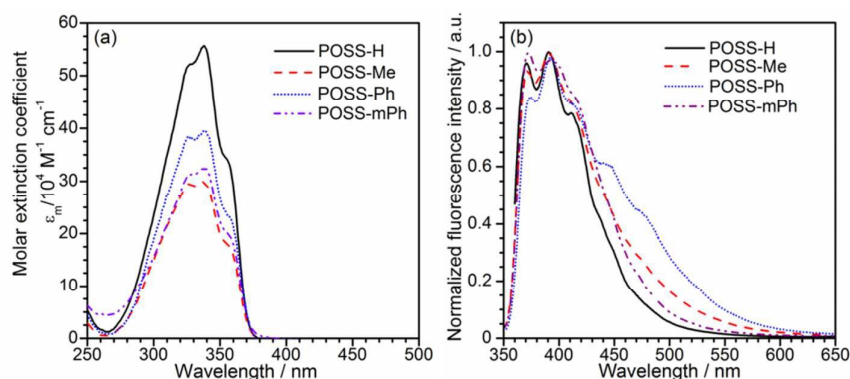
Fig. 2 UV-Vis absorption (left) and fluorescence emission (right; λ_{exc} = 340 nm) spectra of **POSS-H**, **POSS-Me**, **POSS-Ph** and **POSS-mPh** in DCM solution at $\sim 1.10^{-6}$ M.

Remarkably, substitution of the carborane moiety with methyl- or phenyl- groups (**POSS-Me**, **POSS-Ph**, **POSS-mPh**) lowers Φ_F; see Table 1. At a first glance this might surprise because further substituents at the carborane moiety are only expected to impact the electronic structure of the emitting state if the principal conjugated segment is short (i.e. styrene) so that their MOs can effectively overlap with those of the carborane;[17e] this is not expected for the vinyl-stilbene chromophores in the current compounds. In order to prove this, we calculated the electronic and optical properties of just one arm (i.e. trimethoxysilyl-vinyl-stilbene-carborane), comparing the unsubstituted with the *ortho*-phenyl-substituted compound (see SI for details). In fact, energy and oscillator strength of the lowest excited state is almost identical in both cases (in fact, the energy is 3.43 eV, just like the lowest fully allowed excited state in **POSS-H**); the transition is described by a simple HOMO→LUMO excitation, where neither HOMO nor LUMO show relevant participation of the carborane moiety a/o the phenyl-substituent, see Fig. 3. To gain further insight in the different Φ_F we measured the

fluorescence lifetimes τ_F reported in Table 1. In combination with Φ_F this allows to extract the non-/radiative lifetimes k_{nr}, k_F via $\Phi_F = k_F \cdot \tau_F$ and $\tau_F^{-1} = k_{nr} + k_F$. The radiative rates k_r are quite high as expected from the molar extinction coefficients ε_m.[23] However, the main differences in Φ_F arises from the non-radiative rates k_{nr}, (see Table 1); this must arise from cooperative interactions of the arms, i.e. the above mentioned aggregation, which enhances effective trapping.[24,25]

Table 1. Photophysical data for POSS hybrids; fluorescence lifetimes τ_F and quantum yields Φ_F of the compounds in DCM solution;[26] calculated radiative and non-radiative rate constants $k_F = \Phi_F/\tau_F$ and $k_{nr} = (1-\Phi_F)/\tau_F$.[27]

Compound	λ_{abs} (nm)	$\varepsilon_m \cdot 10^{-4}$ ($M^{-1} \cdot cm^{-1}$)	λ_{em} (nm)	Φ_F	τ_F^a (ns)	k_F (ns^{-1})	k_{nr} (ns^{-1})
POSS-H	338	58.1	391	0.59	0.82	0.65	0.54
POSS-Me	338	29.2	391	0.24	0.80	0.29	0.96
POSS-Ph	338	39.3	392	0.21	0.33	0.64	2.39
POSS-mPh	338	33.6	391	0.36	0.83	0.43	0.77

[a]Intensity-average from bi-exponential fit.
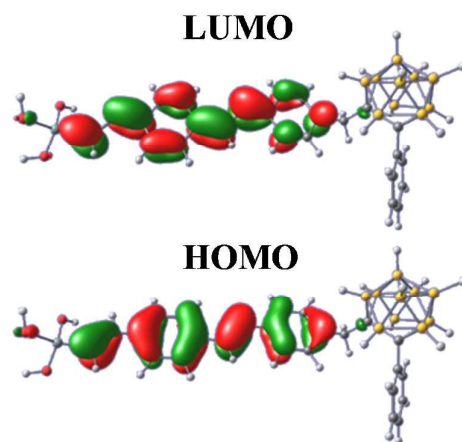
Fig. 3 DFT-calculated frontier MOs of *ortho*-phenyl-substituted trimethoxysilyl-vinyl-stilbene-carborane.

Moreover, the UV-Vis absorption and fluorescence spectra were recorded in solid state films for all compounds (Fig. 4). The UV-Vis spectra exhibit only slight changes in the absorption spectra when compared to DCM solution, with maxima at around 335 nm. Nevertheless, a significant red-shift of about 54-93 nm was found for the fluorescence emission maxima with respect to the solution values, as well as an unstructured spectra (Table 2). Similar effects were previously reported by Laine et *al.* for carborane-free stilbenylsilsesquioxanes.[28] Significantly, the absolute Φ_F in the solid state are only 4-7 % (Table 2), i.e. much lower than in solution (Table 1). Although a small increase in the fluorescence lifetimes τ_F is observed for all POSS films (0.94-1.26 ns), the resulting radiative rates k_F (Table 2) are significant lower compared to those in solution. These observations give clear evidence of considerable intermolecular interactions in the solid state, despite the small changes in the absorption properties.[29]
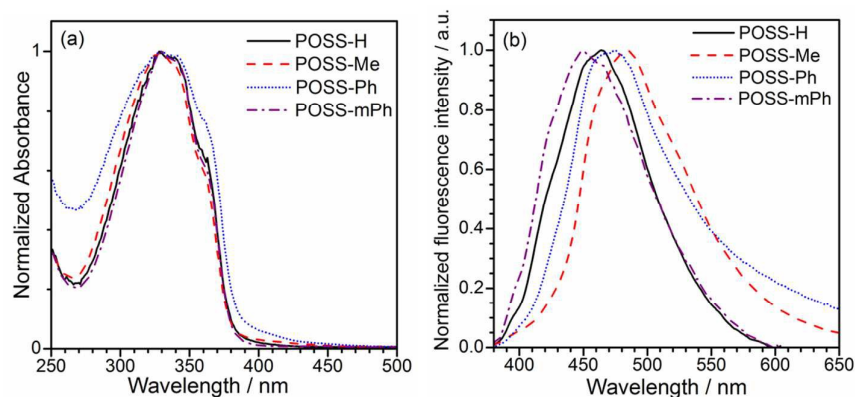

Fig. 4 UV-Vis absorption (left) and normalised fluorescence emission (right; excitation wavelength 340 nm) spectra of **POSS-H**, **POSS-Me**, **POSS-Ph** and **POSS-mPh** drop-casted films.

Table 2. Fluorescence lifetimes τ_F and quantum yields Φ_F of the drop-casted films; calculated radiative and non-radiative rate constants $k_F = \Phi_F/\tau_F$ and $k_{nr} = (1-\Phi_F)/\tau_F$.

Compound	λ_{abs} (nm)	λ_{em} (nm)	Φ_F	$\tau_F{}^a$ (ns)	k_F (ns^{-1})	k_{nr} (ns^{-1})
POSS-H	329-339	464	0.07	1.15	0.06	0.81
POSS-Me	329-339	484	0.06	0.94	0.06	1.00
POSS-Ph	329-339	475	0.06	1.15	0.05	0.82
POSS-mPh	329-339	450	0.04	1.26	0.03	0.76

^{a}Intensity-average from bi-exponential fit.

Thermal Stability. Thermal gravimetric analyses (TGA) were monitored under nitrogen atmosphere at heating rates of 10 °C/min for OVS and carboranyl-substituted vinylstilbenes-containing POSS. The TGA of POSS hybrids show a very different thermal behaviour when compared to the non-functionalized OVS (Fig. 5), indicating that OVS decomposes around 200-300 ºC with a 82 % of weight loss,[4b] whereas carboranyl-containing POSS are stable up to 400 ºC; beyond this temperature a very small weight loss takes place; Table 3 summarises the thermal decomposition and the residues after heating up to 1000 ºC under N_2 atmosphere, showing little changes in the 380-600 ºC range for carboranyl-containing POSS, to produce a residue of 83-87% of the initial weight. Therefore, there is a high preservation degree of the initial mass of the materials described herein. As for previous boron clusters-containing POSS,[10a, 10c] this thermal behaviour confirm that linking carboranyl-substituted clusters to the OVS dramatically increases the thermal stability of the POSS hybrids.

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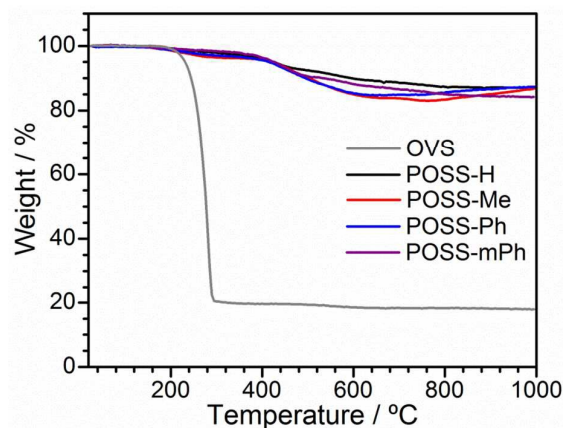
Fig. 5 TGA curves of starting OVS and the final compounds **POSS-H**, **POSS-Me**, **POSS-Ph** and **POSS-mPh** registered under N_2 atmosphere above 120 ˚C, after performing an isotherm step at this temperature to remove adsorbed molecules.

Table 3. Starting decomposition temperature and residue at 1000 ℃ from TGA.

Compound	T (ºC)	Residue (%)	Organic part (%)	Hydrogen (%)
POSS-H	406	86.9	52.73	6.09
POSS-Me	410	86.8	54.30	6.36
POSS-Ph	402	87.3	60.27	5.97
POSS-mPh	408	84.2	60.27	5.97

Conclusions

A new set of octasilsesquioxane-based hybrids decorated with eight carborane-vinylstilbene fragments have been synthesised, isolated and fully characterised. Different C_c-substituted *o*- and *m*-carborane clusters were prepared to assess the influence of both carborane's isomer and the C_c substituent on the photoluminescence properties. Remarkably, the linkage of the carborane cages maintains or significantly enhances the fluorescence emission in solution with respect to non-functionalised POSS

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vinylstilbene derivatives. Modulations of the fluorescence quantum yield (Φ_F) are observed among the different components, reaching $\Phi_F \approx 60\%$ for the unsubstituted *o*-carborane system (**POSS-H**). Nevertheless, in the solid state the emission is largely quenched and bathochromically shifted as a result of considerable intermolecular interactions. All hybrids also exhibit an outstanding thermal stability with a very small weight loss. All these properties make the hybrids excellent candidates as luminescent materials.

Experimental Section

Materials. All reactions were performed under an atmosphere of dinitrogen employing standard Schlenk techniques and 1,4-dioxane was purchased from Merck and distilled from sodium benzophenone prior to use. Commercial grade tetrahydrofuran, methanol were used without further purification. Compounds 1,2-*closo*-$C_2B_{10}H_{12}$ and 1-CH_3-1,2-*closo*-$C_2B_{10}H_{11}$ were supplied by Katchem Ltd. (Prague) and used as received. 1-C_6H_5-1,2-*closo*-$C_2B_{10}H_{11}$, 1-C_6H_5-1,7-*closo*-$C_2B_{10}H_{11}$, Octa(p-bromostyrenyl)silsesquioxane and compounds **1-4** were obtained following literature procedures.[17b, 17e, 19, 30] 4-vinylbenzyl chloride, *n*-BuLi solution (1.6 M in hexane), 4-Bromostyrene, [$Pd_2(dba)_3$] and [[Pd(^{t}Bu$_3$P)$_2$] were purchased from Aldrich and NCy_2Me from Acros. All of them were used as received without further purification.

Instrumentation. Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. ATR-IR spectra were recorded on a high-resolution spectrometer FT-IR PerkinElmer Spectrum One. The ^{1}H NMR (300.13 MHz), ^{11}B{^{1}H} and ^{11}B NMR (96.29 MHz) and ^{13}C{^{1}H} NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer, whereas the ^{29}Si{^{1}H} NMR (59.62 MHz) spectra were recorded on a Bruker 400 MHz spectrometer. All NMR spectra were recorded in $CDCl_3$ at 25ºC. Chemical shift values for ^{11}B{^{1}H} NMR spectra were referenced to external BF_3·OEt_2, and those for ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz. The thermal analyses were performed on a simultaneous thermogravimetric analysis

(TGA) - differential scanning calorimetry/differential thermal analysis (heat flow DSC/DTA) system NETZSCH -STA 449 F1 Jupiter, and a differential scanning calorimeter (power compensation DSC) Perkin Elmer DSC8500 LAB SYS (N5340501) equipped with a Liquid N_2 controller CRYOFILL (N534004). Samples for thermogravimetric characterisation were placed in open alumina crucibles. A heating rate of 10 ºC/min was used and all samples were studied between 40 and 1000 ºC.

Absorption and photoluminescence (PL) measurements: The UV-Vis absorption spectra were performed in spectroscopic grade DCM solutions (Sigma-Aldrich) with concentrations of $\sim 1.10^{-6}$ M in normal quartz cuvette having 1 cm path length; to obtain absorption maxima in the range 0.1-0.2 at the excitation wavelength. Experiments in the solid state were completed in thin films that were performed upon drop casting the THF solutions on quartz surface upon slow solvent evaporation at room temperature. Absorption spectra of solutions and the solid state were measured by a Varian Cary-50 Bio UV-visible spectrometer after proper base line correction. Fluorescence emission and excitation for solutions and films were performed by Fluoromax-4 spectrophotometer (Horiba), equipped with a Xenon high pressure lamp source and double monochromators for excitation and emission. The emission and excitation spectra were corrected for the wavelength sensitivity of the PMT, and the excitation source, respectively. For display in the energy scale, the emission spectra were λ^2 corrected for constancy of the integrated area. Fluorescence quantum yields were determined by comparison using a solution of quinine sulfate in 0.5 M H_2SO_4 with $\Phi_F =$ 0.55 as a standard.[26] Absolute fluorescence quantum yields were determined in an

integrating sphere setup (Hamamatsu C9920) equipped with a xenon high-pressure lamp and a multichannel analyser at 350 nm excitation wavelength.

TCSPC measurements: Time resolved fluorescence lifetime measurements for solutions and films were done by the time correlated single photon counting (TCSPC) technique using a using an Acton SP2500 spectrometer, and low dark current photomultiplier (PMA 06, PicoQuant) for detection. A HydraHarp-400 TCSPC event timer with 1 ps time resolution was used to measure the fluorescence decays. The excitation source was a 337 nm NanoLED (PicoQuant, PLS-8-2-651; 0.5 microwatt power; Trigger level 10 MHz at 90 % intensity) with FWHM ~250 ps. The decay time data was fitted after de-convolution with the IRF data by Fluofit software (PicoQuant).

Calculations. Geometries of the ground and relevant electronic excited states of POSS-H and un-/phenyl-substituted trimethoxysilyl-vinyl-stilbene-carborane were calculated at the (TD)DFT level of theory; for POSS-H, the highest non-planar symmetry (D_2) imposed. The B3LYP functional and 6-311G* basis set was used in all cases as described in the Gaussian 09 program package.[31]

Synthesis of POSS-H: A 5 mL round-bottomed flask under nitrogen was loaded with Octa(*p*-bromostyrenyl)silsesquioxane (50 mg, 0.027 mmol), $Pd[P(t\text{-}Bu_3)]_2$ (2 mg, 0.004 mmol), $Pd_2(dba)_3$ (2 mg, 0.002 mmol) and $1\text{-}[CH_2C_6H_4\text{-}4'\text{-}(CH{=}CH_2)]\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ (**1**) (83 mg, 0.319 mmol). The solids were dissolved in 1,4-dioxane (2 mL), followed by the addition of NCy_2Me (0.15 mL, 0.679 mmol) and stirred at 85°C overnight. The reaction mixture was filtered through 1 cm Celite, washed with 10 mL of THF and the solvent was removed under vacuum. The oily

residue was redissolved in 1 mL of THF, then 15 mL of CH_3OH were added and the precipitated solid was filtered and washed with 10 mL of CH_3OH giving a yellowish solid identified as POSS-H. Yield: 55 mg, 62%. ^1H NMR ($CDCl_3$): δ = 7.53-7.50 (m, 48H, C_6H_4), 7.42 (d, 8H, ^3J(H,H) = 21 Hz, CH=CH-Si), 7.15 (d, 16H, ^3J(H,H) = 9 Hz, C_6H_4), 7.13 (s, 16H, Ph-CH=CH-Ph), 6.38 (d, 8H, ^3J(H,H) = 21 Hz, CH=CH-Si), 3.54 (s, CH_2), 3.27 (s, C_c-H); ^1H{^{11}B} NMR ($CDCl_3$): δ = 7.53-7.50 (m, 48H, C_6H_4), 7.42 (d, 8H, ^3J(H,H) = 21 Hz, CH=CH-Si), 7.15 (d, 16H, ^3J(H,H) = 9 Hz, C_6H_4), 7.13 (s, 16H, Ph-CH=CH-Ph), 6.38 (d, 8H, ^3J(H,H) = 21 Hz, CH=CH-Si), 3.54 (s, 16H, CH_2), 3.27 (s, 8H, C_c-H), 2.33 (s, 21H, B-H), 2.24 (s, 40H, B-H), 2.08 (s, 19H, B-H); ^{11}B NMR ($CDCl_3$): δ = -2.85 (br, 8B), -5.71 (br, 8B), -9.14 (d, 32B, ^1J(B,H) = 149 Hz), -10.98 (d, 16H, , ^1J(B,H) = 175 Hz), -12.80 (d, 16H, , ^1J(B,H) = 204 Hz); ^{13}C{^1H} NMR ($CDCl_3$): δ = 148.75 (s, CH=CH-Si), 137.77 (s, =CH-C_6H_4), 137.45 (s, =CH-C_6H_4), 136.94 (s, =CH-C_6H_4), 133.70 (s, -CH$_2$-C_6H_4), 130.23 (s, C_6H_4), 129.18 (s, CH=CH), 128.20 (s, CH=CH), 127.45 (s, C_6H_4), 127.09 (s, C_6H_4), 126.93 (s, C_6H_4), 117.43 (s, CH=CH-Si), 74.48 (s, C_c-CH$_2$), 59.40 (s, C_c-H), 43.28 (s, CH$_2$); ^{29}Si NMR ($CDCl_3$): δ = -78.18; ATR-IR (cm^{-1}): $\tilde{v}$ = 2578 (s, B-H st), 1599 (m, C=C st), 1090 (br s, Si-O st); elemental analysis calcd for $C_{152}H_{200}B_{80}O_{12}Si_8$: C 55.18, H 6.09; found: C 55.53, H 6.11.

Synthesis of POSS-Me: The procedure was the same as that for POSS-H; Octa(*p*-bromostyrenyl)silsesquioxane (51 mg, 0.027 mmol), Pd[P(*t*-Bu$_3$)]$_2$ (2 mg, 0.004 mmol), Pd$_2$(dba)$_3$ (2 mg, 0.002 mmol), 1-[CH$_2$C$_6$H$_4$-4'-(CH=CH$_2$)]-2-CH$_3$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (**2**) (90 mg, 0.328 mmol), NCy$_2$Me (0.1 mL, 0.453 mmol) in 1,4-dioxane (2 mL); After workup, **POSS-Me** was obtained as a yellowish solid. Yield: 62 mg, 66%. ^1H NMR ($CDCl_3$): δ = 7.53-7.37 (m, 56H, C_6H_4 and CH=CH-Si), 7.20 (d, 16H,

^3J(H,H) = 6 Hz, C$_6$H$_4$), 7.14 (s, 16H, Ph-C*H*=C*H*-Ph), 6.37 (d, 8H, ^3J(H,H) = 18 Hz, CH=C*H*-Si), 3.49 (s, 16H, C*H*$_2$), 2.19 (s, C$_c$-C*H*$_3$); ^{1}H{^{11}B} NMR (CDCl$_3$): δ = 7.53-7.37 (m, 56H, C$_6$H$_4$ and C*H*=CH-Si), 7.20 (d, 16H, ^3J(H,H) = 6 Hz, C$_6$H$_4$), 7.14 (s, 16H, Ph-C*H*=C*H*-Ph), 6.37 (d, 8H, ^3J(H,H) = 18 Hz, CH=C*H*-Si), 3.49 (s, 16H, C*H*$_2$), 2.30 (s, 20H, B-*H*), 2.23 (s, 20H, B-*H*), 2.19 (s, 24H, C$_c$-C*H*$_3$), 2.11 (s, 40H, B-*H*); ^{11}B NMR (CDCl$_3$): δ = -5.85 (d, 16B, ^1J(B,H) = 155 Hz), -10.48 (d, 64B, ^1J(B,H) = 133 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 148.73 (s, *C*H=CH-Si), 137.97 (s, =CH-*C*$_6$H$_4$), 137.04 (s, =CH-*C*$_6$H$_4$), 136.84 (s, =CH-*C*$_6$H$_4$), 134.43 (s, -CH$_2$-*C*$_6$H$_4$), 130.70 (s, *C*$_6$H$_4$), 128.83 (s, *C*H=CH), 128.44 (s, CH=*C*H), 127.39 (s, *C*$_6$H$_4$), 126.83 (s, *C*$_6$H$_4$), 126.69 (s, *C*$_6$H$_4$), 117.35 (s, CH=*C*H-Si), 74.97 (s, *C*$_c$), 41.00 (s, *C*H$_2$), 23.67 (s, *C*H$_3$); ^{29}Si NMR (CDCl$_3$): δ = -78.14; ATR-IR (cm^{-1}): $\tilde{v}$ = 2580 (s, B-H st), 1600 (m, C=C st), 1088 (br s, Si-O st); elemental analysis calcd for C$_{160}$H$_{216}$B$_{80}$O$_{12}$Si$_8$·1H$_2$O·0.5 CHCl$_3$: C 55.10, H 6.25; found: C 55.05, H 6.26.

Synthesis of POSS-Ph: The procedure was the same as that for POSS-H; Octa(*p*-bromostyrenyl)silsesquioxane (50 mg, 0.027 mmol), Pd[P(*t*-Bu$_3$)]$_2$ (2 mg, 0.004 mmol), Pd$_2$(dba)$_3$ (2 mg, 0.002 mmol), 1-[CH$_2$C$_6$H$_4$-4'-(CH=CH$_2$)]-2-C$_6$H$_5$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (**3**) (108 mg, 0.321 mmol), NCy$_2$Me (0.1 mL, 0.453 mmol) in 1,4-dioxane (2 mL); After workup, **POSS-Ph** was obtained as a yellowish solid. Yield: 45 mg, 43%. ^{1}H NMR (CDCl$_3$): δ = 7.75 (d, 16H, ^3J(H,H) = 6 Hz, C$_6$H$_5$), 7.54-7.46 (m, 56H, C$_6$H$_4$ and C*H*=CH-Si), 7.43 (t, 24H, ^3J(H,H) = 9 Hz, C$_6$H$_5$), 7.12 (s, 16H, Ph-C*H*=C*H*-Ph), 6.85 (d, 16H, ^3J(H,H) = 6 Hz, C$_6$H$_4$), 6.42 (d, 8H, ^3J(H,H) = 18 Hz, CH=C*H*-Si), 3.13 (s, C*H*$_2$); ^{1}H{^{11}B} NMR (CDCl$_3$): δ = 7.76 (d, 16H, ^3J(H,H) = 9 Hz, C$_6$H$_5$), 7.54-7.46 (m, 56H, C$_6$H$_4$ and C*H*=CH-Si), 7.43 (t, 24H, ^3J(H,H) = 9 Hz, C$_6$H$_5$), 7.12 (s, 16H, Ph-C*H*=C*H*-Ph), 6.85 (d, 16H, ^3J(H,H) = 6 Hz, C$_6$H$_4$), 6.42 (d,

8H, ^3J(H,H) = 18 Hz, CH=C*H*-Si), 3.13 (s, 16H, C*H$_2$*), 2.78 (s, 20H, B-*H*), 2.46 (s, 25H, B-*H*), 2.29 (s, 35H, B-*H*); ^{11}B NMR (CDCl$_3$): δ = -3.87 (d, 16B, ^1J(B,H) = 136 Hz), -10.16 (d, 64B, ^1J(B,H) = 81 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 148.84 (s, *C*H=CH-Si), 137.94 (s, C$_c$-*C$_6$H$_5$*), 136.79 (s, =CH-*C$_6$H$_4$*), 136.79 (s, =CH-*C$_6$H$_4$*), 136.79 (s, =CH-*C$_6$H$_4$*), 134.72 (s, -CH$_2$-*C$_6$H$_4$*), 131.53 (s, C$_c$-*C$_6$H$_5$*), 130.94 (s, CH=*C*H), 130.85 (s, C$_c$-*C$_6$H$_5$*), 130.47 (s, *C$_6$H$_4$*), 129.12 (s, C$_c$-*C$_6$H$_5$*), 128.65 (s, *C*H=CH), 127.44 (s, *C$_6$H$_4$*), 126.86 (s, *C$_6$H$_4$*), 126.51 (s, *C$_6$H$_4$*), 117.28 (s, CH=*C*H-Si), 83.79 (s, *C$_c$*-C$_6$H$_5$), 82.06 (s, *C$_c$*-CH$_2$), 40.74 (s, *C*H$_2$); ^{29}Si NMR (CDCl$_3$): δ = -78.16; ATR-IR (cm^{-1}): $\tilde{v}$ = 2579 (s, B-H st), 1599 (m, C=C st), 1087 (br s, Si-O st); elemental analysis calcd for C$_{160}$H$_{216}$B$_{80}$O$_{12}$Si$_8$·1H$_2$O·0.5CHCl$_3$: C 59.67, H 5.83; found: C 59.69, H 5.82.

Synthesis of POSS-mPh: The procedure was the same as that for POSS-H; Octa(*p*-bromostyrenyl)silsesquioxane (33 mg, 0.018 mmol), Pd[P(*t*-Bu$_3$)]$_2$ (2 mg, 0.004 mmol), Pd$_2$(dba)$_3$ (2 mg, 0.002 mmol), 1-[CH$_2$C$_6$H$_4$-4'-(CH=CH$_2$)]-7-C$_6$H$_5$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (**4**) (57 mg, 0.170 mmol), NCy$_2$Me (0.1 mL, 0.453 mmol) in 1,4-dioxane (2 mL); After workup, **POSS-mPh** was obtained as a yellowish solid. Yield: 45 mg, 65%. ^{1}H NMR (CDCl$_3$): δ = 7.53-7.45 (m, 48H, C$_6$H$_4$), 7.39-7.36 (d, 32H, ^3J(H,H) = 9 Hz, C$_6$H$_4$ and C$_6$*H$_5$*), 7.26-7.21 (m, 32H, and C*H*=CH-Si and C$_6$*H$_5$*), 7.13 (s, 16H, Ph-C*H*=C*H*-Ph), 6.37 (d, 8H, ^3J(H,H) = 18 Hz, C*H*=CH-Si), 3.29 (s, C*H$_2$*); ^{1}H{^{11}B} NMR (CDCl$_3$): δ =7.53-7.45 (m, 48H, C$_6$H$_4$), 7.39-7.36 (d, 32H, ^3J(H,H) = 9 Hz, C$_6$H$_4$ and C$_6$*H$_5$*), 7.26-7.21 (m, 32H, and C*H*=CH-Si and C$_6$*H$_5$*), 7.13 (s, 16H, Ph-C*H*=C*H*-Ph), 6.37 (d, 8H, ^3J(H,H) = 18 Hz, C*H*=CH-Si), 3.29 (s, 16H, C*H$_2$*), 2.92 (s, 16H, B-*H*), 2.51 (s, 24H, B-*H*), 2.33 (s, 24H, B-*H*), 2.20 (s, 16H, B-*H*); ^{11}B NMR (CDCl$_3$): δ = -6.11 (br, 16B), -10.76 (d, 48B, ^1J(B,H) = 141

Hz), -12.97 (br, 16B); $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ = 148.71 (s, CH=CH-Si), 136.74 (s, C$_c$-C_6H$_5$), 136.53 (s, =CH-C_6H$_4$), 136.47 (s, =CH-C_6H$_4$), 136.47 (s, =CH-C_6H$_4$), 135.26 (s, -CH$_2$-C_6H$_4$), 130.28 (s, C$_c$-C_6H$_5$), 128.57 (s, C$_c$-C_6H$_5$), 128.44 (s, C$_c$-C_6H$_5$), 128.27 (s, C_6H$_4$), 127.78 (s, C$_c$-C_6H$_5$), 127.39 (s, CH=CH), 127.39 (s, CH=CH), 126.78 (s, C_6H$_4$), 126.63 (s, C_6H$_4$), 117.28 (s, CH=CH-Si), 42.94 (s, CH_2); ^{29}Si NMR (CDCl$_3$): δ = -78.17; ATR-IR (cm^{-1}): $\tilde{v}$ = 2594 (s, B-H st), 1599 (m, C=C st), 1091 (br s, Si-O st); elemental analysis calcd for C$_{160}$H$_{216}$B$_{80}$O$_{12}$Si$_8$: C 61.32, H 5.97; found: C 61.31, H 5.94.

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Conflict of interest

The authors declare no conflict of interest.

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Table of Contents Entry

Fluorescent carborane-vinylstilbene functionalised octasilsesquioxanes: synthesis, structural, thermal and photophysical properties

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"The functionalization of POSS with vinylstilbene-carborane moieties leads to tunable fluorescent hybrids with an outstanding thermal stability"